THE INVESTIGATION OF FULLERENE BASED CATALYSTS FOR METHANE ACTIVATION

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ABSTRACT

Prompted by the interesting and unusual chemical activities exhibited by fullerenes, we began an investigation of fullerenes and fullerene soots for converting methane into higher hydrocarbons. We plan to ultimately study fullerene supported metal catalysts for this purpose. However, currently we are investigating the reactivity of various fullerene materials without metals for methane activation. These materials include a fullerene soot, a fullerene soot which has been extracted to remove the soluble fullerenes, like C_{60} and C_{70}, CO_2-activated soot, as well as other carbons such as a Norit-A carbon. We found that fullerene soot activates the C-H bond of methane, allowing methane conversion at lower temperatures (lower by 250°C) than found under purely thermal conditions. Furthermore, soot catalysis appears to produce a minimal amount of aromatic hydrocarbons. The extraction of C_{60}/C_{70} from the fullerene soot was found to reduce the selectivity for C_2 hydrocarbons, while the CO_2 activation of soot does not appear to alter the catalytic activity of the soot. The effect of reaction conditions such as temperature, residence time, added hydrogen and inert gas on the reactivity and selectivity of these materials are presently being studied.

INTRODUCTION

Methane is one of the most abundant sources of energy and is found naturally in underground reservoirs and as a by-product of indirect coal liquefaction and petroleum processes. However, methane has not been successfully utilized because of difficulties in storage and transportation. Conversion of methane into higher hydrocarbons would substantially increase its utilization, and intense efforts have been directed towards this goal. The main difficulty in converting methane is the production of undesirable side products. Oxidative methods easily convert methane to higher hydrocarbons, but over oxidation to CO_2 makes it an uneconomical method. Alternatively, simple thermal decomposition of methane also makes higher hydrocarbons; however, the production of liquid fuels from methane by this method is not yet economically feasible because of the high C-H bond strength of methane compared with that of reaction products (ie. 98.2 kcal/mol for ethane). At the high temperatures required to activate methane, the C_2 products formed will further decompose and produce still higher hydrocarbons, aromatics, and coke.

Direct coupling of methane can be achieved thermally without catalyst. The key to these pyrolysis reactions is to generate methyl radicals, which then polymerize into higher hydrocarbons. However, current methods are thought to produce the radicals in the gas phase, which may lead to indiscriminate reactions and coke formation. In contrast, fullerenes, which have a great affinity for radicals, are expected to add methyl radicals and thereby provide for more selective reactions.[1] Another attribute of these fullerenes is that they can easily incorporate metals either inside or outside the cage structure.[2,3] Some of these metals may impart to the fullerenes properties that will aid in producing methyl radicals. A second reason why fullerenes may be effective catalysts for methane activation is their strong electrophilic character. Recent work shown by Sen et al.[4] has shown that methane may be activated by electrophilic agents. C_{60} and C_{70} fullerenes display remarkable electrophilic characteristics including direct amination with primary and secondary amines and a very low first reduction potential of -0.5 V (vs. NHE). Wudl[5] has characterized fullerenes as, "electrophiles par excellence." In the present study we are evaluating the feasibility of using fullerene based catalysts for methane activation. The full scope of the reactivity of these novel materials is not yet known. Because of the reasons cited above, we believe that catalysts based on C_{60} and other fullerenes will provide a facile pathway to convert methane into higher hydrocarbons.

In the arc process for preparing fullerenes, one obtains C_{60}, C_{70} and other extractable fullerenes along with a much larger amount of an insoluble soot. This soot most likely results from carbon clusters that did not close into fullerenes, but instead continued to grow into large particles. We therefore suspect that the soot so generated also has a fullerene like structure and exhibits many of its properties. We report here the preliminary results on the methane activation catalyzed by this arc generated soot containing C_{60} and C_{70} and compare the results with those obtained with activated carbon (Norit A). We also report on the effect of extracting the soot with toluene, or activating it by partial oxidation with CO_2.

Batch hydrogen and methane activation experiments were conducted by charging a 5 mL tubular reactor with soot and 500 to 1000 psig of gaseous material for 2 hours. The methane activation experiments were conducted using flowing methane at atmospheric pressures. The catalyst was supported on a fritted disk in a quartz reactor. The exit of the reactor was fitted with a quenching zone through which cooling gases could be introduced. The catalyst was heated using a dual furnace reactor system where the methane was first heated in a preheating furnace (at 600°C) and then passed into a high temperature furnace with a short heating zone (4"), leading to the cool quenching zone to minimize any possible thermal reactions after conversion. Soot (containing 12 % C_{60}/C_{70}) was obtained from Ulvick Industries, Inc. Toluene-Extracted soot was obtained from Materials & Electrochemical Research (MER) Corporation. Norit A activated carbon was obtained from Aldrich (750 m^2/g). Carbon dioxide activation was carried out using the procedure described by Tsang et al[6] by treating the fullerene soot or extracted soot with CO_2 (20mL/min) at 850°C for five hours, Surface area of the materials were measured by BET method using N_2. Surface area of the soot and extracted soot were determined to be 125 m^2/g and 185 m^2/g, respectively. The surface areas of the CO_2-activated fullerene soot and extracted soot were found to approximately 600 m^2/g for each material. The gaseous products were analyzed by a Carle CGC 500 gas chromatograph using a TCD detector. Argon was used in the methane gas stream as an internal standard. Fullerene soot, which was subjected to either methane or hydrogen, was analyzed using a surface analysis by SRI's surface analysis by laser ionization instrument (SALI).

RESULTS AND DISCUSSION

The batch experiments were conducted in order to determine the reactivity of the fullerene soot to methane and hydrogen. Analysis by SALI showed that the hydrogen reacted with the C_{60} contained in the soot to produce various hydrogenated C_{60} species; however, no evidence was found for addition of methane to the C_{60} under these conditions. However, since C_{60} was able to "activate" the 104-kcal/mol H–H bond, it seems reasonable that C_{60}, and other fullerenes, can also activate the 105-kcal/mol C-H bond in methane. One possible explanation for the lack of detection of methylated species is that any methane that does react with the fullerene in this batch system will be further decomposed to carbon and not be observed. Thus a continuous reactor system would be a better test of the reactivity of fullerenes for methane activation.

In order to test the effect of fullerenes, we used a high temperature flow through reactor with a minimal heating zone in order to prevent subsequent reactions of the reaction products. For these tests we used fullerene soot and, for comparison, an activated carbon (Norit A) under typical methane activation conditions (600°C to 1100°C). Carbons have been noted to have catalytic activity for methane activation and thus would provide a good comparison for the effect of fullerenes and fullerene soot.[7] During the thermal pyrolysis of methane without catalysis, the formation of tar in addition to coke and gaseous products was observed. However, in the case of fullerene soot or Norit catalyzed methane activation, no tar was observed. Figure 1 shows the extent of methane conversion for the soot, Norit A, and the thermal case (no catalyst) when subjected to flowing methane gas at 100 mL/min. As seen in this figure, when induced by thermal pyrolysis without catalyst, the onset of the methane activation was 900°C, while the onset was observed to be approximately 800°C for the Norit-A and as low as 600°C for the fullerene soot. It is interesting to note that the fullerene soot with a substantially lower surface area (ca. 120 m^2/g compared to 750 m^2/g for Norit A carbon) lowered the onset temperature for methane conversion over that found for Norit A. Hence, the surface area of the carbon is not the discriminating factor. SALI analysis of the fullerene soot after exposure to methane under these reaction conditions, (Figure 2) shows evidence of methylated C_{60}, further demonstrating the capability of soot to activate methane.

The selectivities of C_2 hydrocarbon observed for methane activation at 950°C under different reaction conditions are summarized in Table 1. In order to alter the selectivities we conducted the methane activation experiments in the presence of hydrogen, and for comparison, the presence of an inert gas, helium. The effect of hydrogen dilution is generally recognized to increase the yield and selectivity of C_2 hydrocarbons.[8-10] These trends are consistent with the observation for the methane activation conducted without catalyst or with Norit carbon as catalyst. In contrast, with the fullerene soot, there appears to be only a minor effect with hydrogen, but a much more pronounced and positive effect with helium. This effect may be key to determining the role that fullerene-soot plays in methane activation.

The comparison of methane conversions catalyzed by fullerene soot and extracted fullerene soot as well as these respective soots treated by CO_2 is shown in Figure 3. The extracted soot was prepared by room temperature toluene extraction of fullerene soot. This extraction process removes the soluble fullerenes like C_{60} and C_{70}. However, in the preparation of the soot by arc process, a large amount of large molecular weight fullerene like structures and incomplete fullerene structures are thought to be present. Most research has focused on the soluble part of the soot and very little information of the insoluble soot is available. As seen in this figure both extracted soot and fullerene soot can activate methane at ca. 600°C, with the extracted soot catalyzing more methane conversion than does the fullerene soot. However, as shown in Figure 4, the selectivity for C_2 hydrocarbons is lower in the case of extracted soot than for the fullerene soot, which suggests more coke formation in the methane activation catalyzed by extracted soot.

The reason for this difference is not clear but it could be attributed to the presence of C_{60}/C_{70} in fullerene soot. It might be argued that C_{60}/C_{70} will evaporate at the temperature that methane activation is carried out. But the possibility that C_{60} undergoes reactions with methane and becomes nonvolatile at this temperature can not be excluded. Alternatively, the process of extraction may alter the behavior of the fullerene soot by an as yet unknown manner. Contact with solvents does markedly increase the apparent density of the material. The reason for this anomaly is now under study.

Tsang et al[6] recently reported that treating extracted soot at 850°C with CO_2 leads to the formation of microporous carbon with high surface area. We therefore prepared the CO_2-activated fullerene soot and CO_2-activated extracted soot in the same manner. The weight loss during the CO_2-activation was 20.3 wt% for the fullerene soot and 19 wt% for the extracted soot. The CO_2-activation was found to increase the surface areas of the soots to over 600 m^2/g from 120 m^2/g for the fullerene soot and from 185 m^2/g for the extracted soot. The methane activation study of these pretreated soots is shown in Figures 3 and 4. We found that although CO_2-activation procedure increases the surface area of the soot dramatically, the methane activation catalyzed by CO_2-activated soot does not show higher conversions under these conditions. On the other hand, the selectivity for C_2 hydrocarbon is slightly improved. The CO_2-activated extracted soot does not show any difference from extracted soot in terms of methane conversion and C_2 hydrocarbon selectivity. Comparing the effect of CO_2 activation with extraction suggests that the difference of surface area is not as important as the nature of the catalyst in the catalytic activities and selectivies for methane activation.

CONCLUSIONS

These results obtained so far show that both activated carbon and fullerene soot appear activate the C-H bond of methane and convert it into higher hydrocarbons, albeit to different extents. Both fullerene soot and extracted soot can lower the onset temperature for methane by ca. 250°C compared to the case without catalyst. This activity provides a good ground for the future work on the catalytic application of fullerene-based materials. We plan to explore these differences for both fullerene and metallized fullerenes in future work on the upgrading of natural gas and related work.

ACKNOWLEDGMENTS

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Table 1 The Pyrolysis of Methane at 950ºC and 100 mL/min

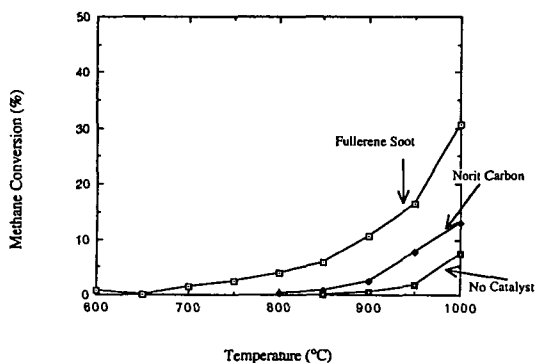| Catalyst Employed	Co-feed Gas (Vol%)	CH_4 Conversion (%)	Selectivity (%)			
			C_2H_4	C_2H_6	C_2H_2	Total
No Catalyst	None	1.7	36	11	8	55
No Catalyst	H_2(50%)	0.3	76	14	0	90
No Catalyst	He(50%)	1	73	0	0	73
Norit	None	7.6	23	2	3	28
Norit	H_2(50%)	0.6	87	6	0	93
Norit	He(50%)	7.3	24	3	3	30
Soot	None	16.9	8	1	1	10
Soot	H_2(50%)	7.4	11	0	0	11
Soot	He(50%)	5	32	5	7	44

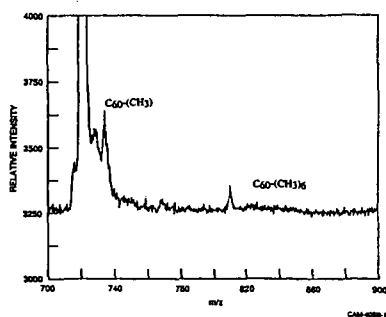Figure 1. Methane conversion as a function of catalyst. Methane flow rate 100 mL/min.

Figure 2. SALI spectrum of fullerene soot treated with methane at 900°C.
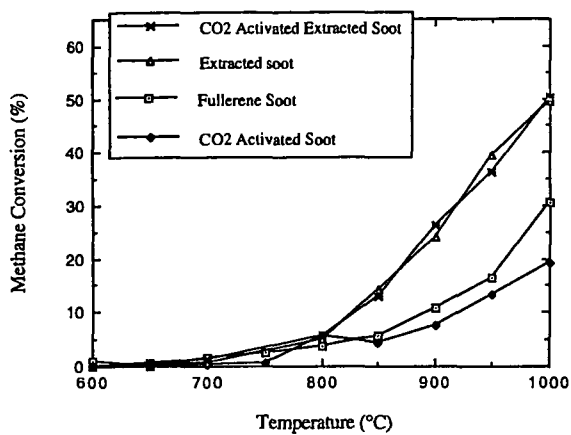
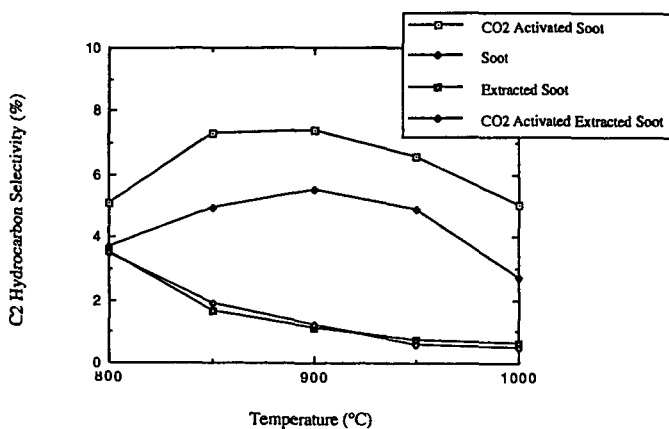Figure 3. Effect of pretreatment of fullerene soot on methane conversion. Methane flow rate 100 mL/min.

Figure 4. Effect of pretreatment of fullerene soot on C_2 selectivity. Methane flow rate 100 mL/min.

Solid Superacid Catalysis: *n*-Butane Conversion Catalyzed by Fe- and Mn-Promoted Sulfated Zirconia

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INTRODUCTION

Environmental concerns are leading to the replacement of aromatic hydrocarbons in gasoline by high-octane-number branched paraffins and oxygenated compounds such as methyl *t*-butyl ether. The ether is produced from methanol and isobutylene, and the latter can be formed from *n*-butane by isomerization followed by dehydrogenation. Paraffin isomerization reactions are catalyzed by very strong acids such as aluminum chloride supported on alumina. The aluminum chloride-containing catalysts are corrosive, and their disposal is expensive. Alternatively, hydroisomerization is catalyzed by zeolite-supported metals at high temperatures, but high temperatures do not favor branched products at equilibrium. Thus there is a need for improved catalysts and processes for the isomerization of *n*-butane and other straight-chain paraffins. Consequently, researchers have sought for solid acids that are noncorrosive and active enough to catalyze isomerization of paraffins at low temperatures. For example, sulfated zirconia catalyzes isomerization of *n*-butane at temperatures as low as 25°C (*1*). The addition of iron and manganese promoters has been reported to increase the activity of sulfated zirconia for *n*-butane isomerization by three orders of magnitude (*2*). Although the high activity of this catalyst is now established (*2, 3*), the reaction network is not known, and the mechanism has not been investigated.

The goal of the research was to investigate low-temperature reactions of *n*-butane catalyzed by iron- and manganese-promoted sulfated zirconia. *n*-Butane was chosen as the reactant because it is a potentially valuable source of *i*-butane.

EXPERIMENTAL

Iron- and manganese-promoted sulfated zirconia was prepared by incipient wetness impregnation from sulfated zirconium hydroxide (Magnesium Elektron, Inc.) that was impregnated with iron and with manganese nitrates. The weight percentages of iron, manganese, and sulfur in the catalyst were 1.0, 0.5, and 1.8 %, respectively.

Before each catalytic reaction experiment, the catalyst in flowing N_2 [30 mL(NTP)/min] was heated from 20 to 450°C at a rate of 7.1°C/min, and the temperature was then held at 450°C for 1.5 h. Reactions were carried out in a once-through plug-flow reactor at atmospheric pressure and temperatures in the range 40-225 °C.

RESULTS

In the absence of a catalyst, no conversion of n-butane was observed. In the presence of the promoted sulfated zirconia catalyst, propane, i-butane, n-pentane, and i-pentane (with traces of methane, ethane, and hexanes) were observed as products. The selectivity for formation of i-butane from n-butane was greater than 85% for conversions less than 60%. At times on stream < 1 h, the carbon balance closed within ±10%, and at longer times on stream this balance closed within ± 5%.

The n-butane conversion as a function of time on stream is shown in Figure 1 for the temperature range 40 to 100°C. There are two distinct regimes, a break-in period followed by a deactivation period. At the lowest reaction temperature, the conversion of n-butane was still increasing even after 4 h on stream. In contrast, at 75°C and at 100°C, the maximum conversion was observed after less than 1 h.

A linear correlation was observed between the maximum n-butane conversion observed in each experiment carried out at temperatures in the range 40-100 °C and the inverse space velocity. Thus the data demonstrate that these conversions are differential and determine reaction rates. However, catalyst deactivation was so fast at the higher temperatures that the maxima in conversion vs. inverse space velocity plots could not be discerned. Thus, the data at these higher temperatures do not determine the maximum conversions. Rates at these higher temperatures were calculated from conversions < 30% on the basis of the assumption that the conversions were still differential.

Rates of formation of the various products at 100°C are summarized Figure 2. Maxima in the rates of formation of each of the following products were observed as a function of time on stream at temperatures < 150°C, provided that the partial pressure of n-butane in the feed was < 0.005 atm: propane, i-butane, n-pentane, and i-pentane. Because of the break-in period, it was not possible to extrapolate these rates accurately to zero time on stream. Thus the values of the rates at the maxima are taken as the best available measures of the initial reaction rates (i.e., those characterizing the undeactivated catalyst).

The predominant product was i-butane, and thus it is concluded that the principal reaction was isomerization of n-butane. The observation of propane and pentanes suggests that disproportionation also occurred. The molar ratio of C_3 to C_5 approached a value of approximately 1.10 ± 0.05 at the lowest temperature investigated (40°C), after about 25 h onstream. Thus these data suggest that stoichiometric disproportionation and isomerization were virtually the only catalytic reactions taking place under these conditions. However, this simple result was not generally observed. Typically, the molar C_3/C_5 ratio was greater than unity. For example, after 3 h on stream at temperatures of 75 to 150°C, the ratio was in the range of approximately 1.5-1.7.

The ratio of C_3 to i-C_4 in the product is taken as an approximate measure of the selectivity for disproportionation relative to isomerization of n-butane. This ratio varied with reaction temperature and time on stream.

As the n-butane feed partial pressure increased, the rate of reaction increased, indicating the positive order of the reaction. Catalyst deactivation was least at the lowest n-butane partial pressure.

DISCUSSION

The data show that conversion of n-butane catalyzed by iron- and manganese-promoted sulfated zirconia at 40 °C gives propane, i-butane, and pentanes as the principal products, along with traces of methane, ethane, and hexanes. By far the predominant product was the isomerization product, i-butane. The same principal product has been observed for n-butane conversion catalyzed by unpromoted sulfated zirconia at 25°C; it was formed along with propane and traces of i-pentane (1). The activity of the promoted sulfated zirconia catalyst is higher than those of the other solid acid catalysts.

Hsu et al. (2) reported the first characterization of the promoted sulfated zirconia catalyst, investigating n-butane isomerization under approximately the same conditions as ours, but with a higher feed n-butane partial pressure (e.g., 0.58 atm). These authors estimated rates of the isomerization reaction by extrapolating conversions to zero time on stream to approximate the performance of the fresh catalyst. Zarkalis (4) investigated a catalyst similar to that of Hsu et al. and estimated activities of the fresh catalyst from the maximum rates measured as a function of time on stream (as in this work). In the work of Hsu et al. and that of Zarkalis, liquid n-butane was used as a feed which was vaporized before introduction into the flow reactor. In the work reported here, the butane was fed as a gas, and the n-butane partial pressures were typically 1-2 orders of magnitude lower than those used by Hsu et al. and Zarkalis. Thus, the rates reported by these workers are not directly comparable to the rates reported here. A rough comparison based on extrapolation of Zarkalis' data shows an order of magnitude agreement with our data.

The simplest product distribution observed in this work is consistent with a reaction network including only isomerization and stoichiometric disproportionation. At the lowest reaction temperature, 40°C, the C_3/C_5 molar ratio after the break-in period was nearly the stoichiometric ratio of unity for disproportionation, namely, 1.1, with an estimated experimental error of about ± 5%. The only other demonstration of a nearly stoichiometric paraffin disproportionation reaction was reported for n-butane conversion catalyzed by aluminum chloride supported on sulfonic acid resin at 100°C; the principal reaction was isomerization, which was much faster than disproportionation (5).

The observation of disproportionation products (5) suggests that a C_8 intermediate might have formed. This same suggestion was made by Bearez et al. (6, 7), who proposed a bimolecular pathway for i-butane conversions catalyzed by H-mordenite at about 350°C. According to their proposal, both the isomerization and disproportionation products could be formed from the C_8 intermediate. Reactions involving C_8 intermediates might be energetically favored over monomolecular isomerization because they would be expected to involve secondary and tertiary carbenium ions, whereas the monomolecular isomerization of n-butane requires the formation of a primary carbenium ion, which is highly unstable (8).

The product distributions at the higher temperatures show that the reaction network must in general be more complex than just isomerization and disproportionation. The observed C_3/C_5 molar ratios were always greater than 1, suggesting the further reaction of C_5 products, which undergo cracking more readily than smaller paraffins (9). The results are not sufficient to demonstrate the stoichiometry of the cracking; they are consistent with the possible formation of C_9 intermediates. Cracking of a C_9 intermediate would give C_3 and C_6 products, among others, and trace amounts of C_6 products were observed. A C_9 intermediate would be formed only from secondary products of n-butane conversion, and therefore it is expected that the concentrations of these species were much lower than those of primary products.

The results suggest that the highly active solid superacid could be a practically useful catalyst for isomerization, which would be accompanied by disproportionation. It could be advantageous to operate at low temperatures to minimize the secondary reactions and to favor the branched isomerization products.

CONCLUSIONS

1. Iron- and manganese-promoted sulfated zirconia is a superacid that catalyzes n-butane isomerization and disproportionation at temperatures in the range of 40°C to 225°C.

2. The predominant reaction was isomerization with the rate of isomerization being 4.2×10^{-8} mol/(s · g of catalyst) with a feed n-butane partial pressure of 0.0025 atm at 75°C.

3. Under the same conditions the rate of formation of propane was 1.2×10^{-9} mol/(s · g of catalyst).

4. As the temperature increased, the selectivity for isomerization decreased and that for disproportionation increased.

5. Following an initial break-in period of about an hour, the catalyst underwent rapid deactivation.

6. The C_5 disproportionation products were partially converted to lower-molecular-weight products; the C_3/C_5 ratio increased with increasing temperature.

7. The solid superacid catalyst is potentially valuable for practical low-temperature paraffin isomerization accompanied by disproportionation of n-butane.

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Figure 1. *Effect of reaction temperature on n-butane conversion catalyzed by Fe- and Mn-promoted sulfated zirconia. Feed n-butane partial pressure = 0.0025 atm at 75°C and 100°C and 0.005 atm at 40°C. Total feed flow rate = 80 mL(NTP)/min. Catalyst mass = 1.5 g.*

Figure 2. *Rate of product formation from n-butane catalyzed by Fe- and Mn-promoted sulfated zirconia. Feed n-butane partial pressure = 0.0025 atm. Temperature = 100°C Total feed flow rate = 80 mL/min. Catalyst mass = 1.5 g.*
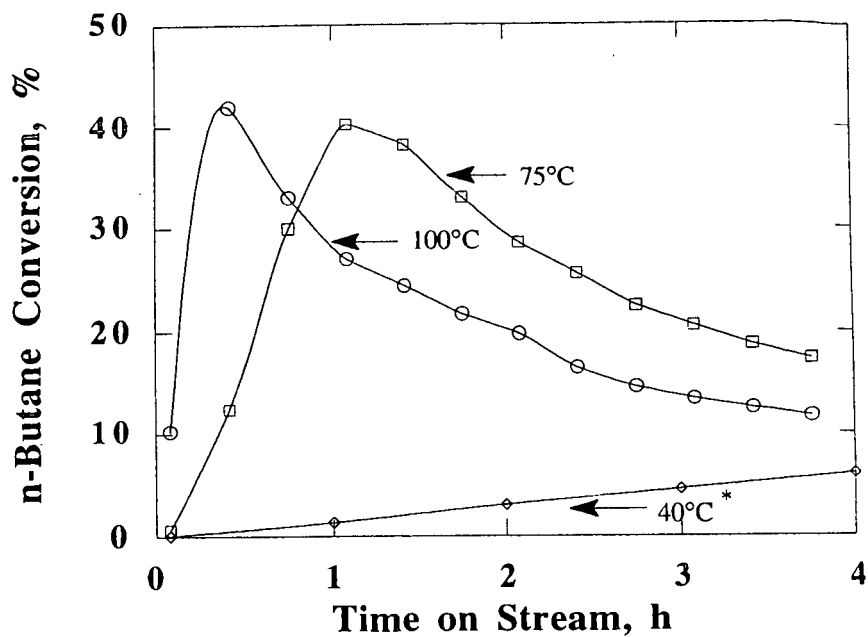
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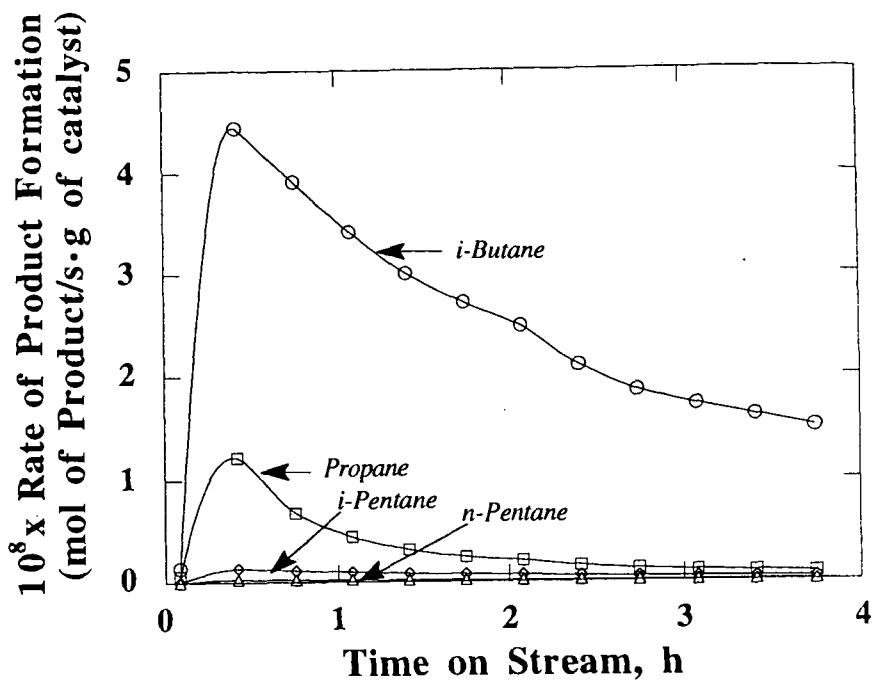
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FEASIBILITY STUDY OF A NOVEL THERMAL
PLASMA PROCESS FOR NATURAL GAS CONVERSION

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KEY WORDS: Thermal Plasma, Pyrolysis, Acetylene

OBJECTIVE
The objective of this research was to conduct a feasibility study on a new process, called
the plasma quench process, for the conversion of methane to acetylene. These efforts were
focused on determining the economic viability of this process using bench scale
experimental data previously generated.

INTRODUCTION
During the last decade most major oil companies have conducted internal studies on
"remote gas" in efforts to capitalize on the large quantities of natural gas known to exist in
various parts of the world. Such studies have typically been directed toward gas resources
which are located too far away from population centers and end-use markets for
conventional use, and cannot be economically liquefied for liquid natural gas carriers.

The Huels Company[1] in Germany has been using a plasma arc process to make light
unsaturated hydrocarbons (acetylene and ethylene) from natural gas since the 1930's.
These light hydrocarbons are subsequently converted to synthetic rubber and liquid
hydrocarbons. The Huels process for arc plasma conversion of natural gas to acetylene
requires quenching of the products by injection of cold liquefied hydrocarbons to prevent
back reactions as the plasma is cooled. Quenching by this method is very energy intensive,
inefficient, and the yield of the light olefin products is relatively low. The single pass yield
of acetylene is less than 40% for the Huels process. Overall process yields are increased to
65% by recycling all of the hydrocarbons except acetylene and ethylene.

Patent protection for this novel process is being pursued by the inventors through the Idaho
National Engineering Laboratory (INEL).[2] Initial work on this process demonstrated
yields of acetylene as high as 70%. Further experiments have resulted in yields greater
than 85% acetylene. Application of catalysts downstream of the quench reactor gaseous
products can convert acetylene to higher molecular weight fractions such as liquid
hydrocarbons.

The PFQR technology overcomes the limitations of other pyrolysis processes by adiabatic
isentropic expansion of gases. Thermochemical modeling studies of the conversion of
methane to acetylene were conducted to determine the equilibrium concentrations of
acetylene and other reaction products between 500 to 3000 K. As expected, these studies
determined that acetylene is a metastable compound that will decompose to carbon and
other hydrocarbons if it is allowed to reach equilibrium at elevated temperatures (>800 K).
The basic concept of the PFQR is that it will maximize the acetylene yield by "freezing" the
product out of the reaction zone with extremely rapid decrease in temperature and pressure.

Successful development of the plasma quench technology (i.e., favorable product
conversion and energy efficiencies) will result in an economic process for conversion of
natural gas to high value hydrocarbons. This technology provide a means for the
petroleum industry to capitalize on the vast quantities of natural gas which are known to
exist (i.e., remote locations and shut-in gas wells) but are not in close proximity to
population centers and thus end-use applications.

PROJECT DESCRIPTION
Historically, methane in non-fuel applications has been limited to feed stock for methanol,
ammonia or hydrogen. With the discovery of natural gas in remote locations, such as, the
North Slope of Alaska, the need for technologies to convert gas to transportable fuels has
arisen. To this date, much of the research effort has been focused on the conversion of natura
gas to methanol (Mobil case) or the oxidative coupling of methane (ARCO Chemical , ACC,
case). LNG is not a viable option in many cases because of the limitations on access to
shipping lanes due to seasonally closed ports or other logistical considerations.

The key variable in the profitability of both the ACC and Mobil technologies is the cost of the
natural gas and the value of the gasoline produced. With the current crude/gasoline pricing,
natural gas cost must be less than $1 per thousand standard cubic feet (MSCF) for an after tax
return on investment (ATROI) of greater than 10%.

RESULTS

METHANE TO GASOLINE ECONOMICS
In this analysis, an alternate route using acetylene from methane pyrolysis is considered. It has been demonstrated that acetylene can be produced from methane in high yields by high temperature, short residence time pyrolysis. Free energy favors the formation of acetylene at high temperatures. Methane pyrolysis has been practiced in the past with varying degrees of success. The major drawback is the inability to raise the temperature of the feed natural gas very rapidly and to quench the products to a non-reacting mixture in less than half of the reaction time.

To avoid the formation of non-selective byproducts via secondary reactions, the products must be quenched very rapidly. Historically, direct quench and direct reactive quench using LPG pyrolysis have been studied in this regard. Recently, the aerodynamic quench has been demonstrated by INEL to provide quenching in under two milliseconds. Acetylene yields have exceeded 90%.

Using this technology and "conventional" hydrogenation and oligomerization catalysts, an economic evaluation was performed. Given the current state of process development, the INEL technology is clearly the low raw material cost and the low cost capital option relative to ACC and Mobil. The estimated capital cost is about 80 % of the nearest competitor, ACC. The leveraging economic variable for the INEL reactor, however, is the amount of power consumed in the pyrolysis reactor and the cost of that power. In the INEL case, the power contribution to required netback can be 50%, easily the largest contributor and over twice the contribution of the cost of the natural gas feed.

The overall economics for the instantaneous construction/operation case indicate that the ACC Redox case is the most attractive for the conversion of natural gas to gasoline. Assuming a 4.5 ¢/kWH power cost and a consumption of 3.6 kWH/lb gasoline for the INEL case, the required netback is 30% greater than the ACC Redox case. With lower cost power, less than 3 ¢/kWH, INEL technology becomes the most attractive of the conversion technologies.

However, the current and forecasted economic situation does not favor using natural gas conversion to make gasoline in any of the processes. Historical data indicate that the refinery gate price of gasoline reaches about $1/gal only when crude rises to $35/bbl. Currently, gasoline and crude oil are much lower, about 60% of these figures. As a target, natural gas would have to be free, when crude is $ 35/bbl in order for the ACC case at 12,500 barrels per standard day (BPSD) to approach a 12% ATROI. There are significant economies of scale that tend to improve the economics substantially, when dealing with large gas fields. The North Slope of Alaska, has a gas supply that would require up to 20 plants of the size evaluated in this report. With these volumes, the ACC technology attains a 12% ATROI when the natural gas price is a maximum of $1/MSCF at $35/bbl crude oil.

With $ 35/bbl crude and a 2 MMMSCFD field, the INEL technology shows break-even economics (12% ATROI, capital USGC basis) at a gas price of $ 1/MSCF, a power cost of 2.5 ¢/kwh and a consumption of 2.5 kWH/lb gasoline. If crude oil prices remain flat on average, as in the 1980's, then the target numbers get more severe.

ALTERNATIVE METHANE CONVERSION TECHNOLOGY
Even given the gloomy economic picture for gas conversion technologies caused by the low crude oil cost, the INEL technology shows significant promise due to low capital cost and high yields. The key process questions that must be addressed are the scalability of the pyrolysis-quench, the reduction in the required power, and the reactor design for the acetylene hydrogenation to insure selective conversion to ethylene rather than ethane.

Developments in the cyclotrimerization of acetylene to benzene provide the possibility of additional improvement in the economics by reducing the capital and operating costs. The downside is the likely inability to use benzene directly as a motor fuel due to environmental and toxicity issues. Since benzene has a higher value than gasoline, the economics could be greatly improved if this market could be exploited. Technologies such as the direct coupled pyrolysis and oligomerization developed at NREL should be investigated. There may be operating conditions in the Plasma- Quench process where the NREL technology may be applicable.

Along the same lines as the benzene argument, the INEL technology may provide an attractive route to ethylene. Rough calculations indicate that the INEL technology is nearly competitive with Ethane/Propane steam pyrolysis. Although much of the US olefin capacity is already in place, there may be another, aggressive round of olefin plant construction in the next two decades, some of which will be based on non-conventional technology. This should be studied in further detail. In order to properly assess the INEL technology in an ethylene case, it is suggested that an entire petrochemical facility be considered based on

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natural gas. Products should include acetylene, ethylene, hydrogen, benzene, ethylbenzene and styrene. All of these products are potentially recoverable in controllable, high yields and with high purity.

CONCLUSION

The major conclusion of this analysis is that the INEL technology could be competitive with existing natural gas conversion technologies given the proper power consumption and pricing. However, none of the technologies will be economical if the predicted long term crude pricing is correct. The INEL technology does have the advantage of providing high yields of valuable chemicals (ethylene and acetylene) at low cost. Downgrading these to gasoline value, although taking advantage of the market demand, reduces the product value significantly and the margins are insufficient to carry the project.

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A Hot-Recycled-Solid Oil Shale Retorting Process For The Production of Shale Oil and Specialty Chemicals

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ABSTRACT

At Lawrence Livermore National Laboratory, we are studying Hot-Recycled-Solid (HRS) oil shale retorting processes through a series of fundamental studies, operation of a 4 tonne-per-day HRS pilot plant and development of an Oil Shale Process (OSP) mathematical model. Over the last two years, under an industrial CRADA with four major oil companies[1], we have completed a series of runs (H10 - H27) using the pilot plant to demonstrate the technical feasibility of the technology, maintain and enhance the knowledge base gained over the past two decades through research and development and determine the follow on steps needed to advance the technology towards commercialization.

The pilot plant, which features no moving parts in critical areas, has been successfully operated for over 100 hours, demonstrating ease of control and reliability of the process. Efficiency is obtained via high throughput, thorough carbon utilization, waste shale heat recovery, improved oil yield and one hundred percent utilization of mined material, including shale fines. We have demonstrated the ability to work with both lean and rich shales (22 - 38 gallons-per-ton), and environmentally the process has superior behavior producing non-hazardous waste shale, minimal sulfur emissions, lower NOx emissions and minimum CO_2 production.

Fundamental laboratory experiments support the pilot plant efforts with determination of kinetics for pyrolysis, combustion and carbonate decomposition for the process as well as determining specifications for produced raw shale oil. In addition, we have developed the Oil Shale Process (OSP) model to aid in critical thinking and scale up of the HRS process.

We have put forth a commercial plant concept which combines the production of refined shale oil, meeting motor fuel specifications, with electric power and specialty chemical production. This plant concept would fully utilize available thermal energy, would solve the waste shale cooling problem and would produce a revenue stream through power and specialty chemical sales which would greatly offset plant operating costs. The net result would be a plant at modest scale (10,000 barrels per day) producing fifty percent specialty chemicals and fifty percent refined motor fuel product[2]. Under this scenario, the motor fuel price required to provide a fifteen percent rate of reutrn on investment would be 71 cents per gallon, which equals the average wholesale price of motor fuel in 1993.

INTRODUCTION

The oil shale deposits in the Western US represent a massive liquid fuel resource, with over 600 billion barrels of recoverable deposits in the Piceance Basin alone. Our objective, together with our CRADA partners, is to demonstrate advanced technology that could lead to an economic and environmentally acceptable commercialization of oil shale.

We have investigated the technical and economic barriers facing the introduction of an oil shale industry and we have chosen Hot-Recycled-Solid (HRS) oil shale retorting as the primary advanced technology of interest. We are investigating this approach through fundamental research, operation of a 4 tonne-per-day HRS pilot plant and development of an Oil Shale Process (OSP) mathematical model.

Over the last three years, from June 1991 to June 1993, we completed a series of runs (H10 - H27) using the 4-TPD pilot plant to demonstrate the technical feasibility of the HRS process and answer key scale-up questions. With our CRADA partners, we seek to further develop the HRS technology, maintain and enhance the knowledge base gained over the past two decades through research and development by Government and industry and determine the follow on steps needed to advance the technology towards commercialization.

One of the crucial challenges in beginning a oil shale industry is how to overcome the high capital cost and long lead time needed to make process improvements which would enable shale oil to compete as a fuel feed stock. We have chosen to focus on an initial plant that converts a large

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fraction of its production into high-valued specialty products to gain an initial market entry. We have determined the economics for a plant producing 10,000 Bbl/day of oil from shale. The plant converts the raw shale oil into a slate of high valued products including specialty chemicals, a shale oil modified asphalt binder and transportation fuels, while co-producing electric power. This small scale venture is shown to be competitive in today's market with a fifteen percent internal rate of return on a capital investment of $725 million dollars. Once in operation, expansion to 50,000 Bbl/day has the potential to become economic through economies-of-scale and cost reductions based on operating experience and plant innovation. This small beginning would provide the operating experience prerequisite for a larger industry, if and when appropriate, that could supply a significant fraction of the US liquid transportation fuel needs.

PROJECT DESCRIPTION

The LLNL 4-tonne-per-day pilot plant consists of a circulating loop and peripheral equipment for the production of oil from shale. Major units of the facility include a fluidized bed mixer, a moving packed bed pyrolyzer, a pneumatic lift pipe and a fluidized bed combustor. Solids are circulated around the loop at 10 kg/min. Fresh shale, crushed to a top size of 7mm, is mixed with hot circulating solids in the fluidized bed mixer. Rapid pyrolysis occurs in 2-3 minutes as the shale passes through the mixer and moving packed bed pyrolyzer. Produced oil vapor, containing water and dust pass through cyclones and filters prior to staged cooling for product recovery. Residual carbon on the spent shale, after pyrolysis, is combusted in the pneumatic lift pipe and fluidized bed combustor, providing the process heat, completing the circulation loop.

Solid flow and bed levels within the circulating loop are maintained using a pair of L-valves, one located below the pyrolyzer and one located below the fluidized bed combustor. Each valve is equipped with a horizontal skid separating inlet and exit by approximately 10 inches. Solids are transported from inlet to exit using gas jets which are pulsed at a frequency of once every 1 to 2.5 seconds. Each pulse moves approximately 250 grams of material. By adjusting the pulse rate and local pressure in the vicinity of the L-valve we achieve a balanced loop at the designed circulation rate, processing 2.5 kg/min of raw shale.

Concurrent to our pilot plant studies is the development of a steady state OSP mathematical model. OSP models each of the major components of the process, allowing us to compute properties and phenomena not readily determined experimentally. The model serves as a critical judge of the experiments and an aid in process scale up. One of the major discrepancies early on between model and experiment was the degree of carbonate decomposition which occurred. To resolve this discrepancy, we have, in the laboratory, reexamined carbonate decomposition kinetics, focusing on the lower temperature ranges typical of our retorting conditions.

OIL SHALE PROCESS MODEL (OSP) RESULTS

We continue to develop our Oil Shale Process model (OSP) as a aid toward process scale up and critical thinking concerning our pilot plant results[1]. OSP is a steady state model, written in FORTRAN, which allows a variety of modules to be coupled together to simulate some overall process. The model consists of three interacting parts: a control portion which handles overall direction of computation and is responsible for coupling process units together through the use of stream variables; a service routine portion which allows common properties to be computed; and any number of modules which do the actual computations associated with a given unit operation. The model defines three types of streams: solid, gas and liquid. All streams have associated with them values for composition, temperature and flow rate. Solid streams are treated as a homogeneous collection of a single specified particle size. Multiple particle sizes are handled by specifying multiple solid streams.

OSP currently contains 13 computational modules. These modules have been kept relatively simple but allow many of the important oil shale physical and chemical processes to be modeled. The modules rely on one of two simplifying assumptions, either one-dimensional co-current flow or complete mixing. The one-dimensional co-current flow construct allows particle/gas systems to be modeled, such as a dense phase moving packed bed, or a dilute phase lift-pipe. The complete mixing construct has utility in modeling fluidized bed systems. Using some combination of these two module types, a variety of unit operations can be simulated.

The moving packed bed pyrolyzer provides a good example of how OSP operates. In this unit, the solids travel from top to bottom in plug flow, while a sweep gas and vapors produced in the bed travel radially from centerline to wall, where vapor removal ports are located. This non co-current gas solid contact is modeled within OSP as a series of well mixed modules coupled from top to bottom to simulate the solid motion.

Under most circumstances, pilot plant results are uses as a guide in verifying modeling assumptions. However, in one case, the discrepancy between model and pilot plant could not be rectified by altering model constructs. This was the case for the measured amount of carbonate decomposition observed from the pilot plant.

LABORATORY EXPERIMENTAL RESULTS

We have recently published retorts of fundamental laboratory experiments in oil coking kinetics[2], char combustion kinetics[3] and flue gas NOx reduction with ammonia addition[4]. Our latest laboratory study focused on carbonate decomposition kinetics.

Decomposition kinetics were measured in the laboratory as an aid in resolving the discrepancy between model and experiment. In the experiments, raw shale was first prepared via slow combustion at low temperature (200 to 350 °C) to remove all of the kerogen while not affecting the initial mineral carbonate concentrations. The prepared sample was then dropped into a fluidized bed and the temperature was ramped from initially 500 °C to 850 °C at 5 deg/min. The evolved CO_2 was measured on a mass spectrometer as a determinate of the rate of carbonate decomposition. Analysis of the dropped sample showed 96% of the carbon to be inorganic. A first order kinetic expression was fit to the experimental data. The kinetics were faster, particularly at low temperatures, compared to previously reported results used in the OSP model. Incorporating these kinetics into OSP has eliminated the large discrepancy between model and experiment.

ECONOMICS AND COMMERCIALIZATION RESULTS

Our commercial concept for the HRS process combines reliability and efficiency with the production of high valued products and minimum environmental disruption. Economics for a 10,000 Bbl/day plant producing a slate of high valued products and co-producing electric power is discussed below.

Development of an efficient, reliable retorting process coupled with pioneering efforts by others in using shale oil as a chemical feed stock for the manufacture of high valued specialty chemicals and for use as an asphalt binder, using the Shale Oil Modified Asphalt (SOMAT)[3] process combine to make for a small scale venture potentially profitable in today's market.

The heart of the 10,000 Bbl/day commercial HRS process is very similar to a combined cycle circulating bed boiler for power production. In this plant, raw shale would first be pyrolyzed to produce oil, followed by combustion of residual carbon to produce thermal energy to drive the process and electric power for on-site use and off-site sale. The power cycle provides a means for spent shale cooling and fuel gas utilization while providing enough revenue to offset the cost of mining the raw shale.

The produced shale oil is split into three fractions. Ten percent is converted into specialty chemicals, unique to shale oil, which could command a sale price of $100/Bbl. The heaviest forty percent is converted into an asphalt binder (SOMAT) for road paving, with a projected sale price of $100/Bbl. The lightest fifty percent is then hydrotreated/refined producing a slate of transportation fuel products ranging from diesel to aviation fuel. The wholesale market price for this transportation fuel mix, averaged in 1993, $.73/gallon or $31/Bbl.

The economics of this 10,000 Bbl/day plant are shown in Table 1. Cost and revenue items are reported on per capacity basis, assuming a 330 day operating year. The capital cost on the $725 million dollar plant with a 15 percent internal rate of return (IRR) on investment equals a capital charge of $37/Bbl. Operating costs including mining, disposal, plant operations and maintenance are estimated by direct comparison with Unocal's operating experience at Parachute Creek. These costs are estimated at $23/Bbl. Hydrotreating/refining costs of $10/Bbl are also based on Unocal's experience, with fifty percent of the product needing hydrotreating in the current plant configuration, this equates to a $5/Bbl cost. The next two operating costs involve conversion of forty percent of the product into a shale oil modified asphalt binder SOMAT and ten percent into specialty chemicals.

Next in the table are the four products from the plant. The first is excess electrical production capacity obtained from the cooling the waste shale and on-site combusting of produced fuel gas. Off-site electrical sales amount to a $5/Bbl credit. The sale of SOMAT and specialty chemicals, each assumed to have a value of $100/Bbl bring in an additional $50/Bbl revenue, leaving a $15/Bbl gap between costs and revenues, with fifty percent of the product left. Here the table deviates from the heading by reporting the required price of the transportation fuel products needed to achieve the fifteen percent rate of return desired. As shown, the required price is about equal to the wholesale price of these fuels during 1993. Thus, the economics for a 10,000 Bbl/day plant have been shown to provide a fifteen percent rate of return on investment in today's market.

Table 2 shows the impact of scale up on economics. As more capacity is added, the capital and operating costs per barrel decline, while revenues from the production of high valued specialty products decline. The required motor fuel price increases to $39/Bbl or $.93/gallon to achieve the desired fifteen percent rate of return, which is a foreseeable rise in fuel price over the next 1-2 decades. In addition, process improvements and innovation based on experience will aid in lowering the overall cost projections for this plant.

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[3] The New Paraho Corporation, Aurora, Colorado.

CONCLUSIONS

Oil shale is one of the most promising alternatives to dwindling petroleum supplies in the US, with over 600 billion barrels of recoverable deposits in the Piceance Basin of Colorado alone. A commercial industry would provide domestic feed stock for specialty chemicals, asphalt binders for longer lasting roads, alternative transportation fuel and electric power at a cost competitive in today's market. A demonstrated technology would provide domestic jobs, aid the US balance-of-payments and give a measure of energy security by serving to cap the price of imported oil and provide an option to partially replace foreign oil in an extended national emergency.

A small-scale industry, today, exploiting high valued products would provide the framework for technological advancement to bringing down the cost for a potential large-scale fuels industry tomorrow. The Government owns most of the resource, and stands to benefit from a commercial oil shale industry through lease and tax revenues. Technical development, however, has been left to industry, with the cost of development proving to be too large for any single company to bear. A small investment by Government, now, could bring into being a small oil shale industry which would pave the way for further development, revenues and jobs in the future.

The LLNL Hot-Recycled-Solid process has the potential to improve existing oil shale technology. It processes oil shale in minutes instead of hours, reducing plant size. It processes all oil shale, including fines rejected by other processes. It provides controls to optimize product quality for different applications. It co-generates electricity to maximize useful energy output. And, it produces negligible SO_2 and NO_x emissions, a non-hazardous waste shale and uses minimal water.

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Table 1. Economics of a 10,000 Bbl/day Plant

Description	Cost & Revenue $/Bbl
Capital cost @ 15% IRR - 725 Million	$37
Unocal's projected operating costs (full production excluding hydrotreating)	$23
Hydrotreat/refine 50% into transportation fuel (cost $10/Bbl)	$5
Convert 40% to SOMAT (seasonal average - cost $5/Bbl)	$2
Convert 10% to specialty chemicals (cost $25/Bbl)	$3
Subtotal - Capital & Operating Costs	**$70**
Off-site electricity sales @ $.03/kWh	($5)
SOMAT asphalt additive @ $100/Bbl	($40)
Specialty chemicals @ $100/Bbl	($10)

Required transportation fuel price for 15% rate of return	**$30**

Transportation fuel wholesale price in 1993	**$31**

Table 2. Economics of a 50,000 Bbl/day Plant

Description	Cost & Revenue $/Bbl
Capital cost @ 15% IRR - 2,225 Million	$23
Operating costs including hydrotreating/refining	$25
Subtotal - Capital & Operating Costs	**$48**
Off-site electricity sales @ $.03/kWh	($5)
SOMAT asphalt additive 15% @ $60/Bbl	($9)
Specialty chemicals 5% @ $60/Bbl	($3)

Required transportation fuel price for 15% rate of return	**$39**

EFFECTS OF SCALE-UP ON OIL AND GAS YIELDS IN A SOLID-RECYCLE FLUIDIZED BED OIL SHALE RETORTING PROCESS

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Keywords: oil shale retorting; fluidized bed; coking and cracking

BACKGROUND
Fluidized bed pyrolysis of oil shale in a non-hydrogen atmosphere has been shown to significantly increase oil yield in laboratory-scale reactors compared to the Fischer assay by many workers.(1,2,3,4) The enhancement in oil yield by this relatively simple and efficient thermal technique has led to the development of several oil shale retorting processes based on fluidized bed and related technologies over the past fifteen years.(5,6,7,8) Since 1986, the Center for Applied Energy Research (CAER) has been developing one such process, KENTORT II, which is mainly tailored for the Devonian oil shales that occur in the eastern U.S.(9) The process contains three main fluidized bed zones to pyrolyze, gasify, and combust the oil shale. A fourth fluidized bed zone serves to cool the spent shale prior to exiting the system. The autothermal process utilizes processed shale recirculation to transfer heat from the combustion to the gasification and pyrolysis zones. The CAER is currently testing the KENTORT II process in a 22.7-kg/hr process-development unit (PDU).

INTRODUCTION
Fluidized bed pyrolysis increases oil yield by reducing the extent of secondary coking and cracking reactions which result in carbonaceous deposition and gas production. The fluidizing gas dilutes the shale oil vapors and sweeps them quickly out of the bed of pyrolyzing shale to reduce both thermal cracking and solids-induced coking and cracking. Fluidized beds, in the case of oil shale retorting, offer an advantage over gas-swept fixed bed reactors because there is little gas/solid contact in the bubble phase of a fluidized bed. Assuming similar fluidization characteristics, the extent of secondary reaction (i.e. oil loss) is affected by bed depth, solid type, and temperature as it is in any gas/solid reaction. For small fluidized beds the bed depth is shallow, so secondary reactions are minimal. Since it is unpractical to increase a fluidized bed to commercial scale by only increasing the cross-sectional area without also increasing the height, an unavoidable increase in secondary reactions will occur with scale up. The extent of this increase can only be reliably determined by experiment because of the difficulty in modeling fluidized bed contacting. Even at the laboratory scale, significant differences in oil yield have been observed as a result of retort size. Rubel and Carter (10) observed that oil yields from a 7.6-cm diameter fluidized bed pyrolyzer were approximately 13% less than the oil yields from an otherwise similar 3.8-cm diameter fluidized bed retort. Increased gas production in the larger retort confirmed that secondary reactions had increased in this study.

Another factor that contributes to high oil yield in small laboratory scale retorts is that the heat for pyrolysis is provided by preheated gas and/or through the walls by an external furnace. In these retorts the nascent shale oil vapors experience contact with

an isothermal and homogenous mixture of pyrolyzing shale. Because processed shale is recycled in commercial-scale retorting schemes, however, the particles in the pyrolysis zone are not homogeneous and may potentially contribute to greater rates of secondary oil-loss reactions compared to pyrolyzed shale particles which have not been additionally processed. Rubel et al. (11) and Coburn and Morris (12) have found that carbon deposition from shale oil vapors is more rapid on combusted shale than pyrolyzed shale. While Udaja et al. (13) found combusted and pyrolyzed shales to have similar propensities for carbon deposition, they also noted that the pyrolyzed shale had a much higher surface area than the combusted oil shale. In general, it appears that oil shale which has had residual carbon burned off via combustion or gasification tends to have higher capacity for carbon deposition. This is consistent with the notion of the "coke clock", first identified by Voorhies (14) in the fluid catalytic cracking literature, where carbon deposits more slowly on cracking catalysts as time of exposure increases (i.e., at higher levels of carbon on the catalyst). Therefore, the oil yield potential of large-scale fluidized bed retorts is potentially affected not only by their size but also by the concentration and composition of recycled shale in the pyrolysis zone.

EXPERIMENTAL

Apparatus. A 7.6-cm diameter, 2.3-kg/hr fluidized bed reactor system has been used extensively at the CAER as a small prototype of the KENTORT II process (15,16) and as an apparatus to study the kinetics of coking and cracking of shale oil vapors over processed shales.(17,18) The prototype is enclosed in electric furnaces to preheat the system and to compensate for heat losses. The PDU (see Figure 1 for flow diagram), on the other hand, operates nearly autothermally and relies on a propane burner to preheat the air entering the combustor and an electric furnace to superheat the steam which fluidizes the cooling, gasification, and pyrolysis zones. In a commercial system the energy for preheating these streams would be recovered in part from cooling and condensing the hot gases and vapors exiting the system. Electric heat tapes surround the pyrolysis zone of the PDU, but provide little net heat to the system. In almost all respects the oil collection systems of the prototype and the PDU are similar. The temperature is reduced in stages which results in a crude fractionation of the oil product. The oil collected in the air-cooled heat exchanger and electrostatic precipitator (ESP) is heavy and viscous and is termed "heavy oil." The oil condensed downstream in the water-cooled condenser is low boiling and is termed "light oil."

Oil Shale Samples. There were two master samples of oil shale that were used in this work. Both are from the Cleveland Member of the Ohio Shale in northeastern Kentucky and are similar in nature except for kerogen content. The average shale analysis for the KENTORT II prototype was: 16.7% C, 2.0% H, 0.7% N, 1.7% S, and 74.5% ash, and the average analysis for the PDU was: 11.3% C, 1.1% H, 0.7% N, 1.8% S, and 82.5% ash. Each master sample was prepared to a size distribution of - 0.85mm +0.25mm.

Operating Conditions. The prototype was run in three different modes of operation: 1) gas heating, 2) gas/solid heating w/o combustion, and 3) gas/solid heating w/combustion. Gas heating runs were performed to establish baseline oil yield data, and the unit was run with and without the combustor in the gas/solid-heating mode to observe the significance of combusted shale on product yields. Throughout the test series, the pyrolysis zone temperature was held at 530-540°C because this temperature

was found to maximize oil yield for this type of shale in a fluidized bed.(19) The gasifier temperature ranged from 750 to 850°C and the combustor from 850 to 910°C. The shale recycle ratio between the gasifier and the pyrolyzer was varied from 1.3:1 to 2.6:1 (recycled shale:raw shale).

Due to its design, the PDU can only operate with all three zones functioning and with shale recycling to transfer heat to the pyrolysis zone. The temperature regimes achieved are similar to those in the prototype: pyrolysis 500-540°C, gasification 700-800°C, and combustion 750-900°C. Due to its larger size, the solid-recycle ratio between the gasifier and pyrolyzer is higher for the PDU and has been recorded in the range of 3:1 to 5:1.

RESULTS AND DISCUSSION

In the gas-heating mode of operation for the prototype, oil yields averaged 129% of the Fischer assay oil yield by weight. Under the most severe solid-recycle conditions (i.e. high recycle rate and temperature) in the second mode of operation, less than 15% oil loss was recorded. Under these conditions approximately 60% of the heat required for pyrolysis was supplied by recirculating shale from the gasification zone. The study was rather inconclusive in determining whether solid-recycle rate or temperature was the more influential parameter; however, it appeared that higher recycle-solid temperatures caused greater oil yield loss. The addition of the combustor to the operation of the prototype did not significantly affect the oil yield. The excess carbon in the shale following pyrolysis and gasification was not completely combusted because the combustion zone was purposefully starved of oxygen. The recycle loop between the combustor and gasifier was undersized, so the heat generated in the combustor with air as the oxidant could not be removed fast enough to maintain the combustor at a materials-safe temperature. Therefore, nitrogen was blended with air to fluidize the combustion zone resulting in partial combustion of the residual carbon. Since the burn out of carbon was not complete, the effect of combusted shale on oil yield in this case was probably masked.

The composite oil produced in the prototype is a heavy, viscous and aromatic material which is composed of 70% "heavy oil" as was described in the experimental section.(20) The character of the oil indicates that minimal secondary cracking and coking has occurred as compared to the oils produced from Fischer assay. There was evidence of increased secondary reactions by a somewhat improved oil quality for the oils produced in the solids-recycle modes of operation. These oils displayed higher H/C ratios, lower viscosities, lower average molecular weights, and an improved boiling range distribution.

Unfortunately, at the time of this writing, complete analyses from the recently successful runs of the KENTORT II PDU are not available, and it is not possible to make quantitative oil yield comparisons to the prototype results. It is fairly certain, however, that the oil yields on a carbon conversion basis are lower than the prototype. A shift to a lighter composite oil is evident because approximately 60% of the total has been collected as "heavy oil." The loss of "heavy oil" is consistent with increased secondary oil-loss reactions because the heaviest and most aromatic fractions are most susceptible to carbon deposition and gas production.

FUTURE WORK

Most PDU runs that have been completed to date have been prematurely shortened because of various mechanical difficulties (ESP failure is most frequent). Therefore, more PDU runs are planned that will attain the design steady-state operating period of ten hours. This amount of time is required so that the solids in the system will reach a steady state composition. Due to the nature of the start-up procedure, all zones of the reactor are composed of combusted shale when raw shale is first introduced. While we do not have a method of on-line oil yield measurement, it is likely that oil generation during this start-up period is very low.

ACKNOWLEDGMENT

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Figure 1.   Simplified flow diagram of the 22.7-kg/hr KENTORT II process-development unit (PDU) at the Center for Applied Energy Research

PROCESSING/ECONOMIC STRATEGY
FOR UPGRADING SHALE OIL

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Keywords: Shale Oil, Chemicals, Separations

INTRODUCTION

Green River Shale Oil (Western U. S.) is comprised of polar compounds, principally nitrogen and oxygen types, and non-polar compounds, principally paraffins, olefins and aromatics. The former may be a valuable source of specialty and fine chemicals while the latter may be refined into fuels and other petroleum products. To take full advantage of the values of the polar types, efficient processes for extraction, conversion and utilization of these types must be developed.

COMPOUND TYPES IN SHALE OIL

The compound types found in shale oil include homologs, analogs and benzologs of pyridines, pyrroles, phenols, amides, ketones, nitriles, carboxylic acids, thiophenes and aromatic hydrocarbons. Some of these types are of extremely high value in their pure form. JWBA estimates that up to 10% of a shale oil barrel may be manufacturable into products of value greater than $1,000/bbl.

ECONOMIC STRATEGY

Figure-1 shows the economic strategy for a value-enhancement venture from shale oil. Because recovery of shale oil has been a long-time historical focus, the technology and economics of retorting are fairly well understood (1). A guaranteed purchase of raw shale oil at $30/bbl (non-hytrotreated) is expected to be sufficient to attract a qualified producer into production.

The intermediate stage of value-enhancement targets both broad-range concentrates and feedstocks for finishing by existing manufacturers of specialty and fine chemicals. In both cases, shale oil becomes a substitute source of feedstock. For broad-range concentrates, shale oil may substitute for coal tars; for specialty chemicals, shale oil intermediates may compete economically with synthetically produced intermediates.

PROCESS STRATEGY

Figure-2 shows a process strategy and a possible suite of products obtainable from shale oil. Shale oil is first separated by a thermodynamically logical sequence by molecular weight and polarity. The non-polar compounds are sent to a conventional petroleum refinery for manufacture of fuels, lube oils and waxes. Heavy ends may be used for asphalt or asphalt blending stock. The use of shale oil for specialty asphalt additives has been previously reported (2).

The polar fractions may be further separated to produce concentrates of specific types. Liquid-liquid extraction may employ acid, base, polar or polar-aromatics solvents. Also, liquid-solid adsorption may be used to isolate specific types.

For large molecules, some form of dealkylation is needed to reduce the molecules to their bare-ring or mildly-methylated form. Hydrodealkylation is one such process which has shown promise. The resulting products are finished into concentrates of specific types that are further processed for production of specialty and fine chemicals.

VENTURE STRATEGY

Before unconventional feedstocks can be incorporated into the marketplace as substitutes for conventional feedstocks or as a source of new products, technology must be developed to exploit potential values found in these materials. There has been relatively little attention paid to utilizing shale oil as a source of nitrogen and oxygen-based molecular types and the prospects for breakthrough discoveries is high.

It is likely that unconventional resources such as shale oil, advanced process coal liquids, tar sand bitumen and biomass will become the source of products with new activities (biological, toxicological, etc.) and properties (materials, polymers, etc.).

Ultimately, an opportunity for profitable investment must be developed. This involves not only price/cost relationships, but also market trends and acceptance of products. Current results show favorable price/cost relationships and markets for potential shale oil products are growing (3, 4). The main task is to actually produce products for inspection and introduction to the buyer. Recent results aimed at achieving these objectives will be reported.

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ACKNOWLEDGMENT

Illustration of Value - Enhancement Sequence

Figure 1.
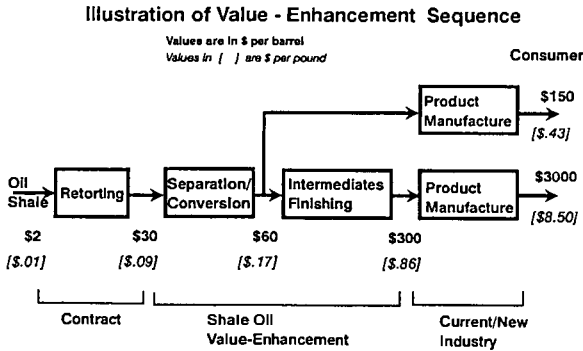
Process Strategy
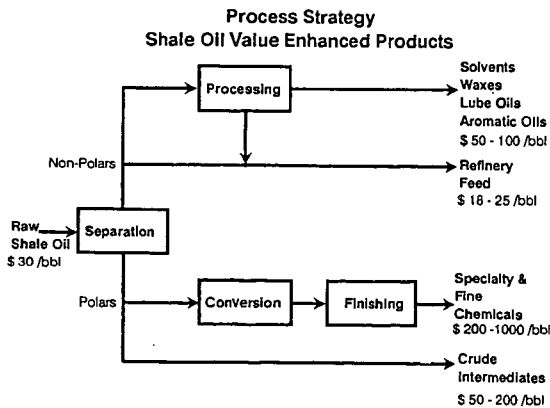### Shale Oil Value Enhanced Products

Figure 2.

THE MEASUREMENT OF PHASE EQUILIBRIA FOR PROCESS STREAMS AT OPERATING TEMPERATURES AND THE IMPLICATIONS FOR THE CRE LIQUEFACTION PROJECT

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Keywords: Phase Equilibria, Liquid Solvent Extraction Process, Coal Solution.

INTRODUCTION

CRE operates the Liquid Solvent Extraction process at its pilot plant in North Wales, UK. The process involves feeding pulverised coal, slurried with a solvent, to a digester in which much of the coal is dissolved. Filtration removes residual solids. The coal solution is fed to an ebulliating bed hydrocracker, together with hydrogen at 200 bar at 425°C. The catalytic reaction adds hydrogen to the coal solution which is distilled to recover solvent and yield a product.

The vessels and pipework are externally heated to ensure that liquids can be pumped but temperatures are not high enough to initiate regressive reactions with consequent formation of carbonaceous solids. However, coal derived liquids are complex mixtures of hydrocarbons which are not soluble in all proportions at all temperatures. Precipitation may occur, leading to blockages in process lines and equipment with subsequent interruption to plant operation. Coal liquids can be regarded simply as a three component system comprising pitch (material with a boiling point >450°C), saturated hydrocarbon (saturates) having a boiling point <450°C and distillate solvent, the remainder of the material boiling below 450°C.

Coal solution, of which LSE reecycle solvent is a particular case, is a mixture of these three components. A study was undertaken to examine the quantity and nature of precipitates formed from coal solutions of various compositions, with a view to preventing plant shutdowns caused by blocked lines.

METHOD

Coal solutions and a coal derived wash oil were selected from appropriate process streams and analysed to determine their pitch and saturates content. The solutions were combined to prepare liquids of varying proportions of distillate solvent, pitch and saturates. The liquid was filtered on a laboratory scale filter rig. (Figure 1) to determine the quantity of precipitate formed.

Coal solution was added to the electrically heated reservoir and allowed to reach a temperature of 200°C. Wash oil was added slowly with stirring to ensure that the temperature of the liquid in the reservoir did not change. Any light material flashing off was collected in a cold trap and returned to the liquid. A 1 bar nitrogen over pressure was applied.

The electrically heated filter body was fitted with a glass fibre filter and allowed to reach 200°C.

On opening the valve the liquid was allowed to pass through the filter paper and the mass of filtrate collected per unit time was recorded. On completion the filter body was dismantled and the mass of precipitate recorded and expressed as a percentage of the total mass of liquid added to the reservoir.

RESULTS

The results were plotted on a triangular co-ordinate system to illustrate a family of curves. Each axis represents one of the three components of the system, distillate solvent, pitch and saturates. Each curve connects points of approximately equal amounts of precipitate (Table 1, Figure 2).

An important property of a triangular diagram is the significance of a straight line joining an apex to a point on the opposite edge. Movement along this line represent a change in the composition of one component while the other two components remain in the same proportions. Therefore as one component is added to the system, the composition of the mixture will always lie at some point on the line.

Figure 3 shows such a system. Lines AA', BB' and CC' drawn from the pitch apex to the opposite base line represents the case where pitch is added to an initial binary mix of distillate solvent and saturates with an initial composition of 80:20, 90:10 and 95:5 respectively. The lines show that as pitch levels increase the quantity of precipitate produced increases to a maximum at approximately 20% pitch and then decreases. The highest level of precipitated material occurs with the highest level of saturates in the mixture.

A typical coal solution will contain slightly more than 40% pitch and a typical LSE solvent some 30% pitch. Figure 3 illustrates the effect of increasing saturates in a typical coal solution (EE') and a solvent (DD').

Within the operating envelope of the plant then as the saturates levels increase the quantity of precipitate produced will continue to increase i.e. up to a saturates level of some 20%.

The nature of the precipitate is reflected in the time that the mixture takes to pass through the precipitate layer on the filter paper. The time taken to filter nominally 100g of the liquid varied and was not related to the quantity of precipitate produced. With the exception of Run 13 which appears to be a rogue result, there is a boundary below which filtration times are of the order of a few minutes and above which filtration rates are much greater. Some precipitates, Runs 6, 8 and 17 blocked the flow completely leaving a quantity of unfiltered material in the filter body. Results for these runs are excluded. For a three component mixture and saturates levels between 2.5% and 20% then this boundary is defined as:-

$$\% \text{ Pitch} = 0.43 \times \% \text{ saturates} + 19. \qquad - (1)$$

If the pitch level in a mixture is less than the value calculated from its saturate content in equation (1), then the precipitate produced will offer only minimal resistance to flow. However, if the pitch level is greater than the calculated value, there will be increasing resistance to flow.

The boundary is shown in Figure 4. For a three component mixture with saturates levels below 2.5% there is minimal resistance to flow. The region within X, Y, Z is a hard brittle precipitate with high resistance to liquid flowing through it.

Mixtures of similar composition were filtered at 225°C, 250°C and 275°C. The results are shown in Table 2. The quantity of precipitate decreased with increasing temperature at a rate of approximately 1% absolute per 25°C rise above 200°C. It would be expected that if a triangular diagram similar to Figure 2, were to be drawn for the three component system at 275°C, there would be a greatly increased envelope in which precipitation would be insignificant and filtration times would also be reduced.

APPLICATION TO PROCESS CONDITIONS

Note: Triangular co-ordinates refer to (% Distillate Solvent, % Pitch, % Saturates).

Case 1
A typical LSE recycle solvent might contain 30% pitch and 10% saturates. If no saturates were present then the composition would be (70, 30, 0). As the saturates increase from 0 to 10%, the amount of precipitate produced rises to approximately 4% at 7% saturates (i.e. 63, 30, 7) and only a further 1% at 15% saturates (55, 30, 15). At this level resistance to flow could be experienced.

On occasions the solvent composition has reached (53, 40, 7) and blockages have occurred in the flow meter in the solvent feed line which is maintained at 150°C. As can be seen on Figure 4, this system would lie in the area where a hard, brittle and low permeability precipitate would form. Precipitation is eliminated at higher temperatures, however this would require replacement of trace heating and flow meters in the line and would increase the power consumption.

Case 2
Wash oil, which is comprised of distillate solvent and saturates only, is pumped along a line, approximately 20m long, to the base of the hydrocracker in order to continually flush the catalyst removal vessel. The line is narrow bore and the flow is 1 kg/hour at ambient temperature. If the flow in the line stops coal solution passes back down the line producing mixtures within a range of composition from wash oil (80, 0, 20) to coal solution (45, 50, 5) causing a precipitate to form. The precipitate will be hard and brittle in nature, Figure 4. Because there is no flow in the line, its surface temperature will increase and the precipitate will form insoluble carbonaceous material and consequently block the line. It was proposed LSE recycle solvent be used as flush oil giving a possible range of compositions in the line from (64, 30, 6) to (45, 50, 5). This avoids the area in which hard precipitate is formed. Further, solvent contains hydrogen donors which help to prevent the regressive reactions which cause coke formation. Since the switch from wash oil to solvent no problems have been experienced in this line.

Case 3
The bearings in the hydrocracker ebullating pumps are flushed with wash oil to both cool the pump bearings and protect it from coal solution. The wash oil re-enters the process steam at 100°C through an oil seal which has a 0.5 mm clearance. No solids can be tolerated in this oil as blockage of the oil seal would cause overheating and subsequent pump failure. Wash oil is chosen for this duty as the components are mutually soluble at these temperatures, no precipitate being present.

CONCLUSION

The mutual solubility characteristics of coal derived liquids can be determined using simple laboratory equipment and may be represented in terms of a three component system. Investigation of such systems have yielded results which have been applied to modify process conditions in a successful attempt to reduce costly interruptions to pilot plant operation.

ACKNOWLEDGEMENTS

Table 1 - Quantity of Precipitate Produced for 3 Component Mixtures

Run Number	% Pitch	% Distillate Solvent	% Saturates	% Precipitate
1	21.4	60.1	18.5	6.0
2	20.4	60.8	18.8	4.8
3	11.9	65.0	23.1	4.1
4	25.1	57.6	17.3	5.4
5	33.4	55.0	11.6	4.9
6	36.4	50.4	13.1	7.7
7	36.8	60.3	2.9	1.3
8	22.7	68.5	8.8	12.0*
9	22.9	71.0	6.2	5.6
10	23.2	73.0	3.8	3.3
11	9.2	78.3	12.5	3.8
12	8.7	82.7	8.6	3.9
13	9.2	86.4	4.5	2.2
14	36.7	59.4	3.9	1.4
15	36.7	58.2	5.0	3.1
16	36.7	59.4	3.9	1.6
17	23.0	70.7	6.3	11.6*
18	9.4	82.1	8.4	3.5
19	3.1	92.5	4.4	1.0
20	6.0	89.9	4.1	1.8
21	14.9	70.4	14.7	5.4
22	17.7	78.1	4.2	3.3
23	4.7	81.0	14.2	2.0
24	11.3	79.6	9.1	3.8
25	35.0	58.0	7.0	5.9
26	25.4	61.9	12.7	4.3
27	15.3	69.2	15.6	4.5
28	20.9	59.3	19.7	8.2
29	31.8	53.9	14.3	4.4
30	38.8	50.1	11.1	4.2
31	10.1	65.5	24.4	2.2
32	16.7	62.0	21.3	4.2

Table 2 - Effect of Temperature on the Quantity of Precipitate Produced

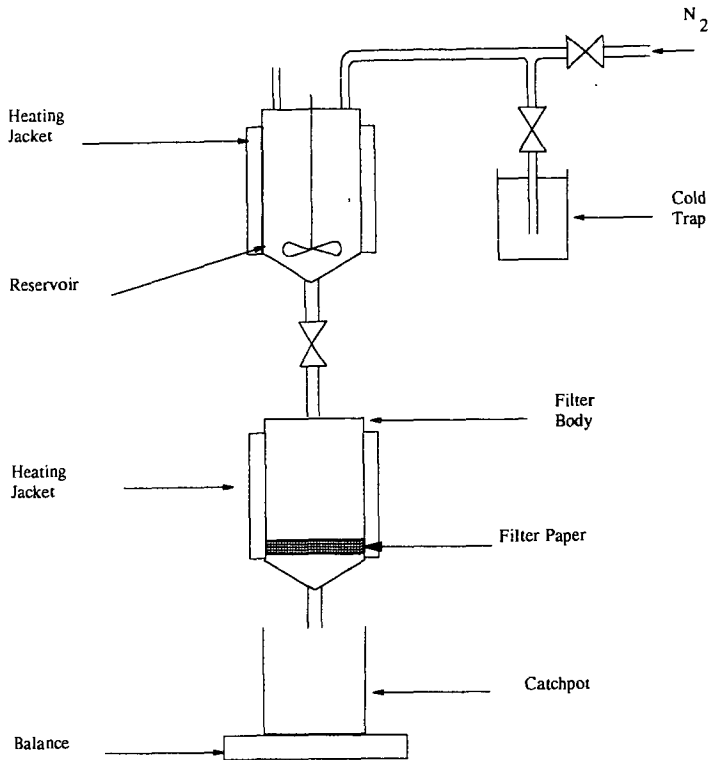| Temp.	% Pitch	% Distillate Solution	% Saturates	% Precipitate	% QI	Filtrate Times (Mins.)	Mass Collected	Comments
225°C	23.4	68.0	8.5	3.0	11.4	2.5	58.1	Brittle
250°C	23.0	68.3	8.7	2.1	20.5	4.5	96.5	Hard
275°C	27.2	68.1	8.7	1.2	46.6	1.2	95.7	Precipitates

Figure 1
Laboratory Filter Rig

Figure 2

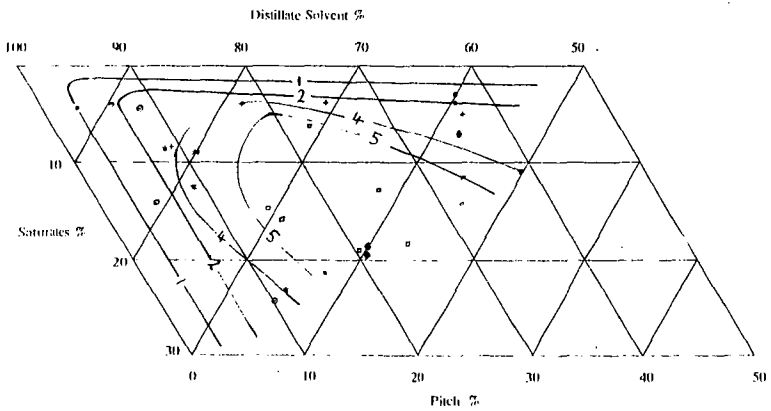Three component system Solvent / Pitch / Saturates at 200°C.

Figure 3

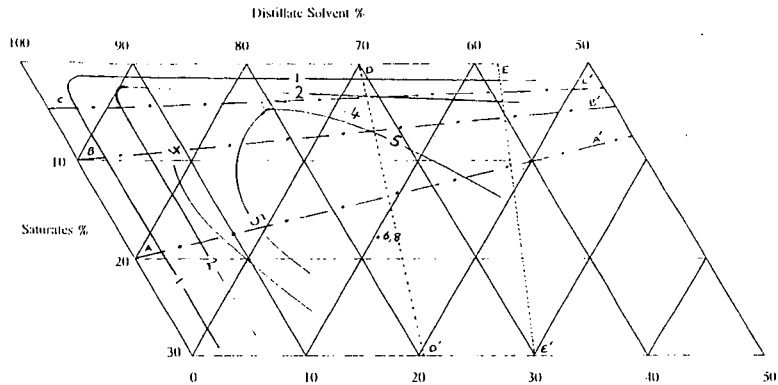Composition of coal solutions for various pitch levels.

Figure 4

Filtration times for the three component system at 200 C